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An Anionic Dimer of Cyclopentadienyl-Titanium (IV) Sulfide: A Potential Precursor for Heterometallic Assemblies

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Abstract

Reaction of $Cp_2Ti(SH)_2$ with lithium salts in THF yields the cluster $Li_6[CpTi(\mu\text{-}S)_3]_2\cdot 6THF$, generated by elimination of CpH. This anionic dimer is unique that during the preparation none of the sulfur atoms of the precursor has been eliminated and the Ti-S-H groups are completely converted to Ti-S-Li bonds. The crystal structure indicates the presence of all Ti-S single bonds in bridging positions of the titanium cluster.

Keywords: Heterobimetallic; Titanium; Cluster; Sulfide; Precursor

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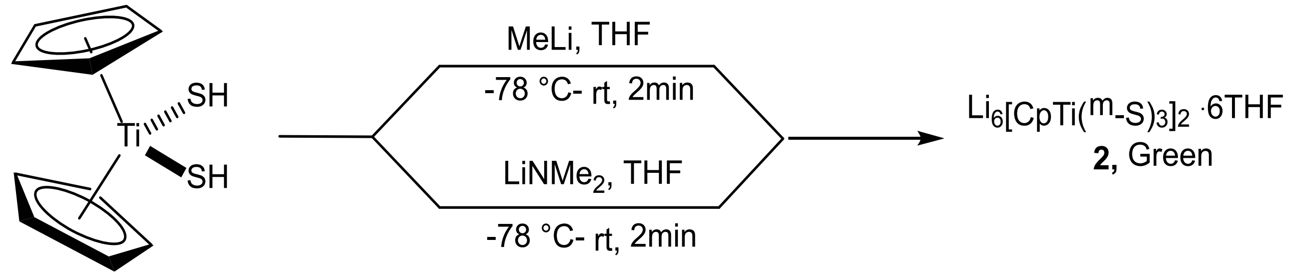
Introduction

Transition metal complexes with bridging sulfide ligands have a broad interest ranging from widely studied biological systems and applied industrial processes, such as hydrosulfurization and catalysis, to novel chemistry of molecular systems [1]. Particularly, complexes having two widely divergent metals, one a Lewis-acid early transition metal and the other an electron-rich late transition metal are promising candidates for new stoichiometric and catalytic reactions [2,3] and they serve as models for studying the role of the support in heterogeneously catalyzed reactions [4]. Multimetallic systems of various main group and transition metals bridged by oxygen, carbon, nitrogen and halides have been reported [5-9]. Properties such as multifunctionality and cooperative effects have been studied [10]. Nevertheless, the problems found to meet the different coordination environments of both metals in close proximity could be as great as the expectations, and thus synthetic strategies leading to new complexes are highly desirable. Although a variety of tetrathiometalates have been very effective in preparing mixed-metal complexes, organometallic early main group metal complexes are relatively uncommon, and efforts to develop their chemistry have been reported recently [11]. Moreover, hydrosulfide complexes that are considered as inorganic equivalents of thiols, can be potential building blocks for the synthesis of sulfur-bridged complexes [12-15] Indeed, most of the hydrosulfide complexes of group 4 transition metals such as $[Cp_2M(SH)_2]$ (Cp) $\eta^5\text{-}C_5H_5$ M = Ti, Zr) react with late transition metal complexes to afford hydrosulfide- or sulfide-bridged complexes. They have described [16] the dimeric species $[CpTi\text{-}(\mu\text{-}S)(S)]_2^{2-}$ while Ref. [17] reported comound $(PhC(NSiMe_3)_2)_2Ti(S)py$. With the exception of these two salts, synthetic pathways to these terminal sulfide complexes involve oxidation of a M(II) species by sulfur. C-S bond cleavage is an alternative route to M-S bond formation. The research groups of Ref. [18,19] have produced TiS and TiS_2 films from titanium thiolate precursors. However, the synthetic approach is not very effective and there is a need for a new synthetic route to prepare sensitive metal thiols. The successful synthesis of terminal hydroxides of Zr, Al, Ge and terminal sulfides of Al, from our group allowed a rational design to assemble novel hetero-bimetallic systems with predictable composition and properties [20-24]. We also reported the lithium salts by reacting hydroxides of Al with $Li[N(SiMe_3)_2]$to afford the novel trimeric lithium-organoaluminate [25]. The utility of this lithium-organoaluminate can be envisaged as alternative precursor, to those of aluminum hydroxides towards the assembly of soluble heterometallic oxides in reactions with metal halides. Similar examples for sulfide complexes are rare compared to those of hydroxides, and in fact no lithium-titanium compounds containing sulfides are known to the best of our knowledge. Organometallic hydrosulfide complexes are potentially valuable to study the development and understanding of metal sulfide based catalysis, especially hydrogenation processes such as hydrodesulfurization. One of the older examples, $Cp_2Ti(SH)_2$, was first synthesized by Köpf and Schmidt in 1965 [26]. The preparation was improved in 1980 by Ref. [27,28] but the reactivity studies of $Cp_2Ti(SH)_2$ in the literature are limited. In our continuing study on the synthesis and reactivity of oxygen/sulfur bridged multimetallic complexes containing titanium [5-9] we have now found that the hydrosulfide complex of a titanium [$Cp_2Ti(SH)_2$)] reacts with lithium amide or methyl lithium to form the lithium salt under elimination of CpH. The resulting compound was characterized by spectroscopic and X-ray diffraction studies. In this paper, we report on the deprotonation of $Cp_2Ti(SH)_2$ by lithium amide to produce an anionic titanium sulfide species of composition $Li_6[CpTi(S_3)]_2$•6THF (**2**). Anionic titanium sulfur containing complexes are rare, and to our knowledge, this dimer is the first reported organometallic lithium-titanium species showing during the preparation the transformation of the terminal Ti-S-H groups to bridging Ti-S-Li bonds. The elimination of CpH from a bis-Cp complex to form a mono-Cp-coordinated Ti is also noteworthy in that $[Cp_2Ti(S)(SH)]^-$ appears to be unstable, while the related $Cp^*_2Ti(O)L$ and $Cp^*_2Zr(S)L$ (L = Py, 4-phenylpyridine, alkyne, alkene) systems are isolable [29-33]. The precursor $Cp_2Ti(SH)_2$ is prepared as published in literature [27,28]. Titanocenebis(hydrosulfide) (**1**) reacts with 1 equiv of $LiNMe_2$ or methyl lithium in THF to produce the anionic titanium sulfide species of composition $Li_6[CpTi(\mu\text{-}S)_3]_2$·6THF (**2**), according to **Scheme 1** [For experimental details, see Supporting Information].

The reaction is slow at low temperature but proceeds very fast at room temperature under changing the color from red to green within 2 min. The color change is accompanied by hydrogen evolution. The complex can be best stored under N_2 atmosphere with cooling in the presence of THF. $Cp_2Ti(SH)_2$ reacts with methyl lithium and $LiNMe_2$, respectively to give compound **2** within 2 min. Both the reactions did not proceed when toluene was used instead of THF at room temperature. However, the reaction was very slow (takes 3 h) and gave a light green product with $LiN(SiMe_3)_2$. Compound **2** was formed, however not in a pure form and is extremely air and moisture sensitive and elemental analysis gave no convincing results. The ^1H NMR pattern is similar to that of the sodium compound $Na_2[CpTi(\mu\text{-}S)(S)]_2$•4THF reported by Ref. [16] although the coordination environment of sulfur at the central titanium is different. The latter exhibits two Ti=S bonds, while compound **2** has only bridging Ti-S-Li units. The NMR-tube scale reaction in THF-d_8, showed the color change within a min. During this period, vigorous effervescence was observed indicating the evolution of a gas. A ^1H NMR spectrum of the resulting solution exhibits the formation of H_2 (δ 4.58 ppm) (Similar peak at δ 4.54 ppm, was reported by Ref. [16]. After some time a resonance around δ 6.00 ppm was observed, this can be attributed to an unknown decomposition product. Furthermore, to confirm the evolution of CpH a sample of the reaction mixture was filtered over alumina and the clear filtrate was collected. This filtrate was analyzed by GC/MS, and only CpH, $[CpH]_2$, and solvent molecules were observed in the spectrum. The spectrum showed no CpH, confirming that the CpH seen in the reaction mixture is not a result of decomposition of the final product, e.g., on the alumina. We obtained 81% yield based on Titanium. In conclusion for the preparation of compound **2** the Lewis base THF seems to be important for the stabilization of the Li cations to compensate the negative charges on the anion. Moreover it is obvious that the deprotonation of $Cp_2Ti(SH)_2$ is faster in polar THF when compared with that in toluene.

Molecular structure of $[CpTiS_3Li_3]_2$·6THF

The green complex crystallizes from THF at -30°C. The THF molecules in the crystal lattice are extremely labile and can be removed in vacuo. The compound crystallizes in the monoclinic P21/n space group [see Supporting Information]. X-ray structural analysis of **2** shows that the species exists as dimer in the solid state and binuclear units are arranged together by weak interactions of bridging sulfide ligands with THF-solvated lithium cations (**Figure 1**). Selected bond lengths and angles of 2 are shown in the caption of **Figure 2**. Unlike the reported sodium titanium cluster [16] compound **2** contains no terminal sulfur atoms which are concurrent with the tendency of the sulfur ligands to bridge metal centers. All the three sulfur atoms are bridged to titanium with Ti-S bond distances of 2.291 Å (av). A comparison of the Ti–S bond lengths of **2** with those of reported Ti–S bond lengths (2.413(2) Å) [8] showed a distinct shortening of the former one. However, these Ti-S distances are slightly longer than the corresponding Ti-S (2.249 Å (av)) bond lengths in the homometallic complex ($Cp_2TiClS_2ClTiCp_2$) [34]. The Li-S (2.463 Å (av)) distance in **2** is comparable with those found in for homometallic complexes (2.401 Å (av)) [35]. The average distance between two metal centers of titanium and lithium is 3.020 Å and the mean bond angle of Ti-S-Li is 79.20°. The Li…Li separation within the Li_3S_3 ring in **2** (av 2.77 Å) is similar to the Li…Li separation within the Li_3O_3 in $[LAl(Me)OLi]_3$ [10]. Apparently the Li^+(THF) network also maintains the integrity of the complex in solution, because decomposition occurs in



Scheme 1 Synthetic route to compound 2.

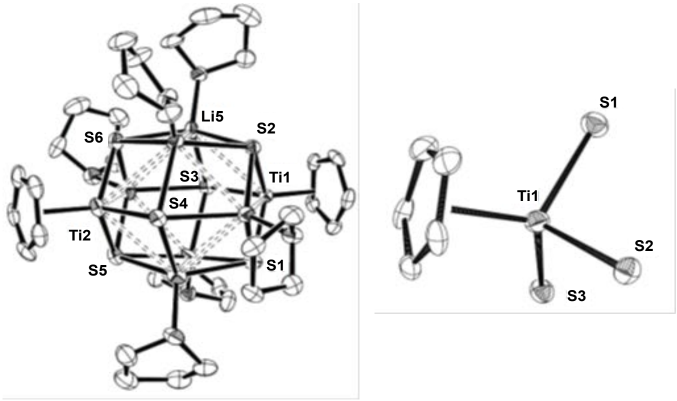


Figure 1 Molecular structure of [CpTiS$_3$Li$_3$]$_2$·6THF and its asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity Selected bond lengths Ti(1)-S(1) 2.299(2); Ti(1)-S(2) 2.290(2), Ti(1); S(3), 2.283(2); Ti(2)-S(4), 2.290(2); Ti(2)-S(5), 2.2949(2); Ti(2)-S(6) 2.305(2). Selected bond angles S(3)Ti(1)S(2), 104.00(7); S(3) Ti(1)S(1), 104.14(8); S(1)Ti(1)S(2) 103.84(8); S(4)Ti(2) S(5) 103.85(8); S(5)Ti(2)S(6), 104.26(8).

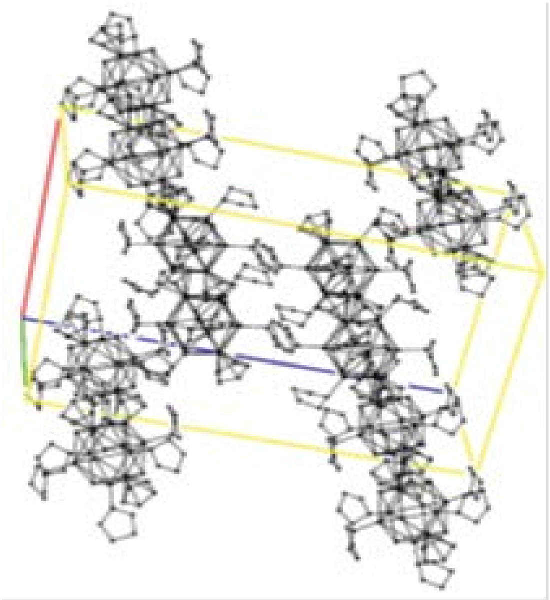


Figure 2 Perspective view of the packing in **(2)** the THF molecules fill the channels between the Ti-S-Li cluster.

solvents other than THF. Each Ti(IV) atom of **2** is six-coordinate but is formally electronically unsaturated. The lithium ion centers are arranged in distorted cube similar to those of methyl lithium [35]. Heterobimetallic sulphide clusters like [CpTi(μ_3-S)$_3$Ir$_3$(μ_2-CO)(CO)$_3${P-(OMe)$_3$}$_3$], have two long (3.121 Å (mean)) and one short (2.815 Å (mean)) Ti-Ir distances [1]. However, in compound **2** distance between the Ti atoms is large indicating that there is no Ti-Ti bond is present, which would be consistent with the apparent d^0 electronic configuration. The unit cell packing shows the importance of THF molecule that fills up the channel between the Ti-S-Li cluster. Recrystallization other than THF was not occurred and decomposition of **2** was observed in toluene. Crystal Packing without THF molecule shows the fewer Ti-S-Li clusters exposing the huge gap between each molecule (see Supporting Information). The Li$_6$[CpTi(μ-S)$_3$]$_2$·6THF cluster was successful isolated and shows in the X-ray single crystal structure the presence of all Ti-S-Li single bonds in bridging positions. Complex **2** provides a rare example of a lithium titanium-sulfide complex with a cyclopentadienyl ligand on each of the titanium atoms. The cyclopentadienyl ligands as well as the THF coordinate lithium ions makes this cluster soluble in THF and therefore might be prone for further reactions under smooth conditions.

Experimental Details

General procedures

All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or using a dry box unless otherwise specified. All chemicals used were of reagent grades and were purified by standard purification procedures. Cp$_2$Ti(SH)$_2$ was prepared as reported elsewhere [1].

Crystallographic analysis

All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. All structures were solved by direct methods and expanded using Fourier techniques [5-9] and the non-hydrogen atoms were refined anisotropic ally. Hydrogen atoms were included but not refined. All calculations for complexes **2** were performed using the crystal structure crystallographic software package [15]. Selected crystal collection parameters are summarized in **Table 1**, and the detailed structure reports including their CIF files shown in the Supporting Information.

Synthesis of 2

5 mmol (**1**.220 g) of titanocene bis(hydrosulfide) (**Scheme 1**) and 1 equiv of (5 mmol, 0.255 g) LiNMe$_2$ were placed in a Schlenk flask with stirrer in a glove box. THF solvent (20 mL) is added and the mixture is stirred at room temperature with the solution changing color from red to green in two min. The color change is accompanied by the evolution of a gas (effervescence). This reaction proceeds very slowly at low temperature. The complex can be best stored under cooling in the presence of THF vapor. Compound **2** is extremely air and moisture sensitive. Yield 0.99 g (81% based on Cp$_2$Ti(SH)$_2$ ^{1}H NMR.

Supplementary Material

Appendix A, CCDC 1430445 **2** contain the supplementary crystallographic data for this paper. Supplementary data to this article can be found online at these data include Experimental details, crystallographic files.

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Table 1 Crystal Data and Structure Refinement for Compound $Li_6[CpTi\ (\mu\text{-}S)_3]_2{\cdot}6THF$ (**2**).

Empirical formula	$C_{34}H_{58}O_6Li_6Ti_2S_6$
Formula weight	892.60
Temperature	100(2) K
Colour	Green
Wavelength (Å)	1.54178
Crystal System	Monoclinic
Space group	*P*21/n
a [Å]	19.4757(10)
b [Å]	10.6671(5)
c [Å]	32.4375(15)
α [deg]	90.00
β [deg]	96.96(2)
γ [deg]	90.00
V [$Å^3$]	6689.0(6)
Z	15
Density (calculated) Mg m^{-3}	1.385
Absorption coefficient (mm^{-1})	4.635
F (000)	2906
θ range for data collection (deg)	2.52 to 58.79
Index ranges	$-21 \le h \le 21, -11 \le k \le 11, -35 \le l \le 35$
No. of reflections collected/unique	Total: 58391 Unique: 9514 (R_{int}=0.1783)
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.067
Final *R* indices ($I>2\sigma(I)$)	*R*1=0.0699, w*R*2=0.1188
R indices (all data)	*R*1=0.1379, w*R*2=0.1392
Largest diff peak/hole [e $Å^{-3}$]	-0.381/+0.636

References

1 Kuwata S, Nagano T, Matsubayashi A, Ishii Y, Hidai M (2002) Sulfur-bridged early-late heterobimetallics synthesized by incorporation of titanium, vanadium, and molybdenum into bis(hydrosulfido) templates of group 9 metals. Inorg Chem 41: 4324-4330.

2 Kuwata S, Hidai M (2001) Hydrosulfido complexes of transition metals. Coord Chem Rev 213: 211-214.

3 Kuwata S, Hidai M (1998) Chem Lett 885-887.

4 Kabashima S, Kuwata S, Hidai M (1999) Electron-Deficient Early−Late Heterobimetallic Sulfido Clusters. Unusual Reactivities of $Ti_2Ru_2S_4$ Cubane-Type Clusters with Four Cyclopentadienyl Coligands. J Am Chem Soc 121: 7837-7840.

5 Kabashima SI, Kuwata S, Ueno K, Shiro M, Hidai M (2000) Crossed Condensation of Two Different Hydrosulfido-Bridged Dinuclear Complexes: Structures and Reactivities of TiRu(3)S(4) Cubane-Type Sulfido Clusters. Angew Chem Int Ed Engl 39: 1128-1131.

6 Hidai M, Kuwata S, Mizobe Y (2000) Synthesis and reactivities of cubane-type sulfido clusters containing noble metals. Acc Chem Res 33: 46-52.

7 Kalck P, Serra C, Machet C, Broussier R, Gautheron B, et al. (1993) Carbonylation of ethene to acrolein in the presence of the early-late heterobimetallic complex [AsPh4][(.eta.5-C5Me5)2Zr(.mu.-S)2Rh(CO)2].cntdot.THF. Organometallics 12: 1021-1023.

8 Kato H, Seino H, Mizobe Y, Hidai M (2002) Syntheses and reactivities of hydrosulfido- or sulfido-bridged heterobimetallic complexes containing Group 6 and Group 9 metals. J Chem Soc Dalton Trans 1494-1497.

9 Casado MA, Ciriano MA, Edwards AJ, Lahoz FJ, Oro LA, et al. (1999) Sulfido-Bridged Tetranuclear Titanium−Iridium Complexes with an Unconventional Tetrahedral Iridium Center. Organometallics 18: 3025-3028.

10 Takii Y, Gurubasavaraj PM, Katao S, Nomura K (2012) Effect of Terminal Aryloxo Ligands in Ethylene Polymerization Using Titanatranes of the Type, [Ti(OAr){(O-2,4-R2C6H2)-6-CH2}3N]: Synthesis and Structural Analysis of the Heterobimetallic Complexes of Titanatranes with AlMe3. Organometallics 31: 8237-8239.

11 Gurubasavaraj PM, Roesky HW, Nekoueishahraki B, Pal A, Herbst-Irmer R (2008) From Unstable to Stable: Half-Metallocene Catalysts for Olefin Polymerization. Inorg Chem 47: 5324-5327.

12 Gurubasavaraj PM, Mandal SK, Roesky HW, Oswald RB, Pal A, et al. (2007) Synthesis, Structural Characterization, Catalytic Properties, and Theoretical Study of Compounds Containing an Al−O−M (M = Ti, Hf) Core. Inorg Chem 46: 1056-1059.

13 Gurubasavaraj PM, Nomura K (2010) Hetero-bimetallic Complexes of Titanatranes with Aluminum Alkyls: Synthesis, Structural Analysis, and Their Use in Catalysis for Ethylene Polymerization. Organometallics 29: 3500-3504.

14 Gurubasavaraj PM, Nomura K (2009) Synthesis and Structural Analysis of Titanatranes Bearing Terminal Substituted Aryloxo Ligands of the type [Ti(OAr){(O-2,4-Me2C6H2-6-CH2)2(OCH2CH2)N}]n (n = 1, 2): Effect of Aryloxo Substituents in the Ethylene Polymerization. Inorg Chem 48: 9491-9495.

15 Delferro M, Marks TJ (2011) Multinuclear olefin polymerization catalysts. Chem Rev 111: 2450-2453.

16 Lundmark PJ, Kubas GJ, Scott BL (1996) Formation of an Anionic Titanium(IV) Sulfido Dimer, {Na2[CpTi(μ-S)(S)]2·4THF}2, by Elimination of CpH and H2 from Cp2Ti(SH)2 upon Deprotonation with NaH. Organometallics 15: 3631-3634.

17 Hagadorn JR, Arnold J (1997) Preparation of Complexes Containing Ti=E, Ti(2)(&mgr;-E)(2), and Ti(eta(2)-E(2)) (E = O, S) Functionalities from a Reactive Titanium Dinitrogen Complex. Inorg Chem 36: 2928-2929.

18 Winter CH, Sheridan PH, Lewkebandara TS, Heeg MJ, Proscia JW (1992) A single-source precursor to titanium nitride thin films. Evidence for the intermediacy of imido complexes in the chemical vapor deposition process. J Am Chem Soc 114: 1095-1097.

19 Bochmann M, Hawkins I, Wilson LM (1988) Thermal deposition of TiS films from volatile Ti(SBut)4. J Chem Soc Chem Commun 344-346.

20 Gurubasavaraj PM, Roesky HW, Sharma PMV, Oswald RB, Dolle V, et al. (2007) Oxygen Effect in Heterobimetallic Catalysis: The Zr-O-Ti System as an Excellent Example for Olefin Polymerization. Organometallics 26: 3346-3349.

21 Gurubasavaraj PM, Roesky (2010) HW Oxygen-Bridged Bimetallic Complex and Polymerization Process. US Patent 8598284.

22 Jancik V, Peng Y, Roesky HW, Li J, Neculai D, et al. (2003) The First Structurally Characterized Aluminum Compound with Two SH Groups: [LAl(SH)2] (L = N(Ar)C(Me)CHC(Me)N(Ar), Ar = 2,6-i-Pr2C6H3) and the Catalytic Properties of the Sulfur P(NMe2)3 System. J Am Chem Soc 125: 1452-1454.

23 Bai G, Peng Y, Roesky HW, Li J, Schmidt HG, et al. (2003) Synthesis, Structural Characterization, and Reaction of the First Terminal Hydroxide-Containing Alumoxane with an [{Al(OH)}2(μ-O)] Core. Angew Chem 115: 1168-1172.

24 Pineda LW, Jancika V, Roesky HW, Neculai D, Neculai AM (2004) Angew Chem Int Ed 43: 1419-1423.

25 Singh S, Chai J, Pal A, Jancik V, Roesky HW, et al. (2007) Base free lithium-organoaluminate and the gallium congener: potential precursors to heterometallic assemblies. Chem Commun (Camb): 4934-4936.

26 Köpf H, Köpf-Maier P (1979) Titanocen-dichlorid - das erste Metallocen mit cancerostatischer Wirksamkeit. Angew Chem Int Ed Engl 18: 477-480.

27 Shaver A, Marmolejo G, McCall JM (1990) Cyclometallapolysulfanes (and Selanes) of Bis(η5-Cyclopentadienyl) Titanium(IV), Zirconium(IV), Molybdenum(IV) and Tungsten(IV). Inorg Synth 27: 65-67.

28 McCall JM, Shaver A (1980) Catenated polysulfur ligands: the pentasulfides of di-η5-cyclopentadienyl-zirconium(IV) and -hafnium(IV)a. J Organomet Chem 193: C37-C40.

29 Carney M, Walsh JP, Bergman RG (1990) Cycloaddition and Cycloreversion Reactions of a Monomeric Ti(IV) Oxo Complex with Terminal and Internal Alkynes. A Reversible Oxametallacyclobutene/Hydroxoacetylide Interconversion. J Am Chem Soc 112: 6426-6429.

30 Polse JL, Andersen RA, Bergman RG (1995) Cycloaddition and Cycloreversion Reactions of a Monomeric Ti(IV) Oxo Complex with Terminal and Internal Alkynes. A Reversible Oxametallacyclobutene/Hydroxoacetylide Interconversion. J Am Chem Soc 117: 5393-5397.

31 Howard WA, Parkin G (1994) Terminal oxo, sulfido, selenido, and tellurido complexes of zirconium, (.eta.5-C5Me4R)2Zr(E)(NC5H5): comparison of terminal Zr-E single and Zr:E double-bond lengths. J Am Chem Soc 116: 606-609.

32 Howard WA, Waters M, Parkin G (1993) Terminal zirconium oxo complexes: synthesis, structure, and reactivity of (.eta.5-C5Me4R)2Zr(O)(NC5H4R'). J Am Chem Soc 115: 4917-4919.

33 Smith MR, Matsunaga PT, Andersen RA, Bergman RG (1993) Preparation of monomeric (Me5C5)2VO and (Me5C5)2Ti(O)(L) and their decomposition to (Me5C5)4M4(.mu.-O)6. J Am Chem Soc 115: 7049-7052.

34 Maué GP, Fenske D (1988) Naturforsch B 43: 1213-1215.

35 Brown TL, Rogers MT (1957) The Preparation and Properties of Crystalline Lithium Alkyls. J Am Chem Soc 79: 1859-1862.